Comment #	Comment by:	Comment	Response
1	ACA (via David Darling)	Lauren – the American Coatings Association (ACA) supports the comments submitted by Jay West of the American Chemistry Council on the Northwest Green Chemistry's draft report to the Spokane River Regional Toxics Task Force on the potential regeneration of PCBs through the TiO2 manufacturing process. We agree that the Hu and Hornbuckle paper presents the most rigorous analysis as compared to other data sources. This paper did not find PCBs in any of the inorganic pigment samples tested and should be discussed and cited in the TIO2 paper. As we discussed, please do not cite ACA in the TIO2 report.	
2	ACC (via Jay West)	Thank you for the opportunity to review Northwest Green Chemistry's draft report to the Spokane River Regional Toxics Task Force on the potential inadvertent generation of PCBs through the chloride manufacturing process for TiO_2. We very much appreciate your active outreach to TiO_2 manufacturers during your research, and we would like to submit the following comments and questions on the draft:	
3	ACC (via Jay West)	1. Is it possible to obtain a copy of the study described in the first paragraph of page 12? We respect that the source may wish to remain anonymous, but it would be useful to understand several things. For example, how were the samples handled prior to analysis to protect them from contamination? Did the samples come directly from a TiO_2 manufacturer, or were they possibly repackaged by a distributor or another entity in the supply chain? If so, there could have been significant opportunity for sample contamination, which would not be reflective of the product when it emerges from the manufacturing process. Is it possible to add additional data and information to put the reported numbers in context?	
4	ACC (via Jay West)	2. EPA Method 1668 was designed to extract/detect PCBs from environmental media and tissue samples ("wastewater, surface water, soil, sediment, biosolids and tissue matrices"; U.S. EPA, April 2010, p. iii). Is a sample of pure TiO_2 sufficiently similar to "soil" such that 1668C is an appropriate test? EPA allows for modifications, as long as the performance criteria specified in the methodology are met. Also, information about the credentials and qualifications of the testing laboratory and chain of custody of the samples was not evident from the paper, leading to questions about the quality and validity of the test results.	

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5	ACC (via Jay West)	3. Questions about handling prior to analysis is also a concern for the Ctistis (2016) paper cited in the report. For example, sample A, was acquired from a paint retailer in the Netherlands (verftechnieken.nl). We can assume that there was at least one repackaging event, and the paper provides no information concerning storage media, storage conditions, etc. The same could be true for the samples from the scientific supply houses. Information about the primary source of the pigments, sampling, handling, and possibility of prior contamination before reaching the lab would be useful in determining whether the PCBs detected came from the TiO2 production process or other sources.	
6	ACC (via Jay West)	4. The publicly available supplementary table to the Hu and Hornbuckle (2010) paper cited in Northwest Green Chemistry's October 2018 report to the Task Force contains data on measured PCBs from samples purchased at three different paint retailers. The authors found no PCBs in any of the inorganic pigment samples. We think the Hu and Hornbuckle paper presents the most rigorous analysis compared to other data sources and has the added benefit of assessing inadvertent PCB content in a real-world consumer product that could be used in the watershed.	
7	ACC (via Jay West)	5. Figure 5 from Ctistis (2016) contains reaction steps that do not exist in industrial chloride processes. For example, hydrolysis of TiCl4 (step 2) is not used to produce pigment grade TiO2. At steps 4 and beyond in the figure, certain reaction materials, energy inputs, and reaction pathways are not found in the industrial chloride process for TiO2 production, making it implausible that PCBs, PCDDs, or PCDFs would be formed in this manner.	
8	ACC (via Jay West)	6. Regarding section 4.2 and the estimate of 576 pounds of inadvertent PCBs from chloride process TiO2, the United States accounts for a little less than 15% of global TiO2 consumption, which corresponds to 86 pounds of inadvertent PCBs for all uses in the U.S. The quantity would decrease precipitously with greater spatial resolution. If one assumes the levels reported in the Ctisis et al. (2016) are from the TiO2 manufacturing process, using those levels would	

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9	ACC (via Jay West)	7. Pure TiO2 is incorporated and bound into the matrix of consumer products, further reducing the potential, if any, for inadvertent PCB contribution to the environment from the TiO2 in those products. Paint and plastic industry products, which the draft report correctly references as the largest uses of TiO2 pigment, typically contain 10% or less TiO2. Understanding the propensity of inadvertent PCBs that might potentially exist to remain bound within the dried, cured paint and in the article matrix itself (rather than leach to the environment) is also important. There is also the possibility that components of paint, plastic, paper, and other products, other than white TiO2 pigment, may contribute PCBs to those products at some level, if any are found.	
10	ACC (via Jay West)	8. The draft report "Spokane River Regional PMF Analysis: Blank Influence Analysis Conceptual Scope of Work" that was prepared for the Task Force also contains useful information. The authors say that "All of the various PMF models suggested that Aroclors are the dominant source of PCBs to the Spokane River" and that PCB 11 is "responsible for a small fraction" (p.22). We searched the report for mention of PCBs 206, 208, and 209, which the state's PCB chemical action plan says are associated with TiO2 (reference to a presentation by Rodenburg, 2012, original reference not available). PCBs 206 and 208 were not detected in 80 or more of the samples taken and were therefore not included in the analysis (p. 12). The authors note a single model run where PCB 209 was associated with a suite of other PCBs that the authors do not attribute to TiO2 (p.19).	
11	ACC (via Jay West)	In conclusion, our members stand by their assertions that their manufacturing processes are not conducive to inadvertent PCB production and, when also taking into account the items detailed above, do not support the need for additional work. The most rigorous study (Hu and Hornbuckle 2010) shows no inadvertent PCBs associated with TiO2, and there are many questions about the other lines of evidence.	
12	ACC (via Jay West)	The one thing I would ask you to look at though in the Hu and Hornbuckle paper. I think you said on the Green Chemistry WG call that they tested a formulated product, so the results weren't directly applicable to your research question. I looked at the paper again, and they say that they tested paint pigment, not paint. The pigment is the powder that's added to the base. They also used a method that is validated for dry particulates only, which confirms for me that they did not test paint. I may be remembering inaccurately, but I thought I'd mention it.	

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13	ACC (via Jay West)	1. Please use the attached slides in the description of the chloride process. Cristal would prefer not to have their logo in the final report. They did not "genericize" the slides previously because they thought they would only be background to the phone conversation, not an insertion into the report. 2. Mark's last name is Pomponi. 3. Doug's last name is Herrmann (two r's, two n's).	
14	Adriane P. Borgias	With regards to Jay's question: If he is referring to the 2012 presentation material provided by Lisa Rodenburg then I believe her conclusions stem from work that she has done in the Delaware River. Here is a link to an article that has an explanation about congener profiles for Titanium Dioxide: https://pubs.acs.org/doi/pdf/10.1021/es400375e Hope this is helpful.	
15	Adriane P. Borgias	Thank you for the thoughtful paper. I have a few comments, they are not substantial and hopefully not too late. As far as broad scale impacts, there are a number of ways the data can be looked at on a per capita basis. Using population data, estimate can be made on how much is used/possibly in the Spokane area. The question of how PCB would enter the river based on use is more nebulous and depend on explicit assumptions, including river flows. One can potentially calculate a mass loading to the river in the parts per quadrillion range. The point being, that I agree with the recommendation that further testing would be worthwhile. A congener profile, which you can get with 1668C could help identify if the pigment has a significant contribution to wastewater concentrations. Perhaps include the profile as a recommendation on page 13?	
16	Adriane P. Borgias	Other specific comments: 1) pg 3 -- "production may be a non-trivial contributor to emissions of inadvertent PCBs" Suggest changing the wording to "non-trivial source" of PCBs.	

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17	Adriane P. Borgias	2) pg 4, para 1 -- "The goal of the Task Force is to develop a comprehensive plan . . . " The Task Force completed this goal. I am wondering if referencing the Vision Statement is more appropriate here. The Regional Toxics Task Force will work collaboratively to characterize the sources of toxics in the Spokane River and identify and implement appropriate actions needed to make measurable progress towards meeting applicable water quality standards for the State of Washington, State of Idaho, and The Spokane Tribe of Indians and in the interests of public and environmental health.	
18	Adriane P. Borgias	3) pg. 9 The Spokane River also exceeds the water quality standards for dioxin (PCDDs) in a couple of locations (https://fortress.wa.gov/ecy/approvedwqa/ApprovedSearch.aspx) -- Search 2,3,7-TCDD and Spokane River. It appears from this paper that addressing this PCB source could also help address a dioxin source.	
19	Adriane P. Borgias	4) pg 4, para 2 -- delete "developing performance-based limits" -- that is not a function of the Task Force.	
20	Adriane P. Borgias	5) Wordsmithing comments · "sulphate" vs. "sulfate": be consistent in the usage -- sulfate is the IUPAC term so probably preferrable; British English is sulphate. · Pg 5 "burnt" should be "burned" (the sentence is in the active tense?) · Pg 7 Table 1. Units? Metric tons? · Pg 12 para 4: "Based on our findings to date, we expect that very low levels will be found" Perhaps this should be should be "levels in the parts per billion range" will be found?	
21	Doug Krapas	it would be a very simple matter to test pure TiO2 from the chloride manufacturing process using EPA Method 1668 to settle this matter once and for all, so we could move onto other potential sources of inadvertent PCBs if they are indeed not present	
22	Mike Petersen	Your white paper is very good and raised excellent questions and thoughts about further research. I know you focused on pigments, but wonder if a paragraph about other products that contain TiO2 would be appropriate. Health care products, colorings in food, and sunscreen in particular have quite a bit of TiO2. I have a sunscreen that says it is 7.5% TiO2, for example and this stuff could be washing	

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23	Doug Greenlund	comments on Draft: The Potential for Generating Inadvertent PCBs through TiO2 Manufacturing Using the Chloride Process Page 3 ...TiO2 production may be a non-trivial contributor to emissions of inadvertent PCBs. This statement needs some reference to why it would be considered non-trivial. 576 pound per year for the entire planet seems small. How does it compare to other sources?	
24	Doug Greenlund	Page 4 first paragraph. These pollutants exceed water quality standards in several segments of the river. The regulation is for total PCB. Should it say "this pollutant exceeds"?	
25	Doug Greenlund	Page 10 Expert claimed that because the TiO2 process is entirely inorganic, Don't they add coke which is carbon produced from the pyrolysis of coal? Seems like there would be plenty of organic starting material there. Even if there was a low level of chlorinated biphenyl production and a high level of destruction, since we are testing for compounds in the low part per billion high part per trillion level the potential is high.	
26	Doug Greenlund	There is a recommendation for testing. We should test both the chlorine based and sulfur based production processes. Make sure we know which process was used in the production. Have enough samples to make statistically valid conclusions. Who is willing to pay for enough testing to make that happen?	